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DETERMINATION OF CERIUM(III)  
BY COULOMETRICALLY GENERATED POTASSIUM MOLYBDICYANIDE

by



RICHARD JOHN PARKER

A THESIS

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THE UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled DETERMINATION OF CERIUM(III) BY COULOMETRICALLY GENERATED POTASSIUM MOLYBDICYANIDE submitted by Richard J. Parker in partial fulfilment of the requirements for the degree of Master of Science.

Date *14 September 1971*



## ABSTRACT

An analytical method was developed for the determination of cerium(III) by oxidation to cerium(IV) in 33 percent aqueous potassium carbonate with coulometrically generated molybdicyanide. Cerium(III) samples in the range 1 to 30  $\mu$ eq were analyzed with a precision of one to three percent. The end point was determined potentiometrically. To compensate for high results caused by the partial decomposition of molybdicyanide, a series of cerium(III) standards were run and a calibration curve was constructed. This calibration curve was linear over the range investigated. Decomposition of the molybdicyanide was reduced but not eliminated by excluding light from the system. The precision of the method decreased when the potassium carbonate concentration was above 40 percent or below 20 percent. No improvement in precision was found when potassium bicarbonate was added to the system to lower the pH.

The analysis of cerium(III) in the presence of a large excess of cerium(IV) is possible. A commercial sample of ceric ammonium sulphate was shown to contain approximately 0.7 percent cerium(III). This result was confirmed by an oxidation-reduction titration following total oxidation of the cerium(III) and an EDTA titration following total reduction of the cerium(IV). Lanthanum(III), nickel(II), zinc(II) and small amounts of iron(III) do not interfere with the titration. Iron(II), manganese(II), chromium(III), vanadium(IV) and cobalt(II) are all oxidized under the experimental conditions employed. Copper(II) interferes with the potential measurement by preventing observation of the potentiometric end point.



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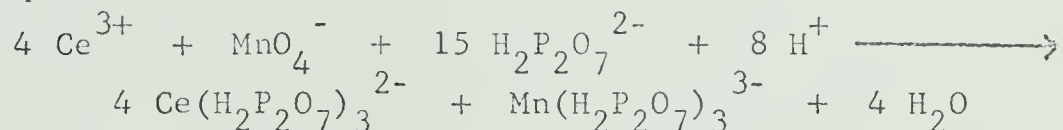
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## INTRODUCTION

Only a few methods are available for the direct analysis of cerium(III) salts. Numerous successful procedures have been employed to oxidize cerium(III) to cerium(IV) where it can be easily determined using a suitable reductant. Although these methods eliminate the rare earths as interferences they are obviously unsuitable when there is a significant amount of cerium(IV) already present in the analyte.

Cerium(III) cannot be directly titrated in acidic media with an oxidizing agent because of the high potential of the cerium(IV)/cerium(III) couple ( $E^0 = +1.44$  volts versus the normal hydrogen electrode in  $1M$   $H_2SO_4$ ). However, in alkaline media or media which enable the cerium(IV) to form stable anionic complexes the potential of the couple is considerably reduced. Thus Goffart<sup>1</sup> was able to successfully oxidize cerium(III) quantitatively with potassium permanganate in neutral pyrophosphate media according to the equation:



It is interesting to note that manganese(III) is the stable state of reduced manganese, making manganese(II) a potential interference. Direct potentiometric end points could not be employed in this titration because of sluggish electrode response near the equivalence point. Goffart therefore suggested an amperometric end point. Hume<sup>2</sup> improved on this work by developing a photometric end point using the absorption at 525 mμ of the excess permanganate. He was able to determine 5 to 80 mg amounts of cerium(III) in large excesses of cerium(IV) with excellent accuracy and a precision of 2 to 4 parts per thousand. Similarly Rao, Rao and Rao<sup>3</sup> were able to determine cerium(III) in  $12M$  phosphoric acid by titration with potassium dichromate. While the potential of the chromium(VI)/chromium(III) couple is also raised in this media the potential break involved in the





titration was small, and time consuming  $dE/dV$  plots were necessary to find the point of inflection of the curve.

It has been known since the middle of the last century that even atmospheric oxygen will oxidize cerium(III) in alkaline media. Several methods using potassium permanganate were proposed but they were of poor reliability. In 1925 Tomicek<sup>4</sup> employed potassium ferricyanide as the oxidizing agent in concentrated solutions of potassium carbonate. His work showed that at least 20 percent potassium carbonate was needed to hold the cerium in solution. Although the method gave satisfactory results the potential break was again small and  $dE/dV$  plots were required. Tomicek's method was sound and only the lack of a sufficiently powerful oxidizing agent or a better end point detection technique limited its usefulness. Thirty years later, Hume<sup>5</sup> investigated the use of an amperometric end point to improve on Tomicek's work. Voltammetry using a rotating platinum electrode indicated 0.0 volts versus the saturated calomel electrode to be the best choice of potential. Although this technique gave a good end point even in the presence of a 100-fold excess of cerium(IV) the results were one half percent low with a precision of one half to one percent.

Ferricyanide in alkaline tartrate media has also been used by Basinka<sup>6</sup> as a titrant for cerium(III). With murexide as indicator he obtained a precision of one half percent in the 1 to 200 mg range. Results were less precise with a potentiometric end point.

Almost simultaneously with Hume's work, Dolezal<sup>7</sup> made a detailed polarographic study of the cerium(IV)/cerium(III) system in carbonate solutions. He did not propose this as a method for the analysis of cerium, however. He showed that the cerium(IV)/cerium(III) couple was reversible, with a half wave potential of -0.158 volts versus the saturated calomel electrode. This work encouraged Dolezal together with Rössler and Zyka<sup>8</sup> to try and find a more suitable oxidant in this medium. They found chloramine T, alkali hypochlorite, iodine, vanadate, and lead tetraacetate unsuitable, but obtained good results with potassium



periodate. The periodate couple has a potential of +0.87 volts at pH 9.2 which decreases with increasing pH until at pH 10.8 it does not give a break in the titration curve. At optimum conditions, pH 9.8, results were good to one percent in the 10 to 50 mg cerium range and 1.8 percent at the 1 to 10 mg level. However, at the periodate concentration employed, 0.01M, 1 mg cerium would require only about 0.7 ml of titrant, so the precision of the method at this level is low. In view of this and the lack of suitable alternative methods of determining cerium(III) at the milligram and submilligram levels a method employing a coulometrically generated oxidant was investigated. The oxidant chosen for this study was not periodate but potassium molybdicyanide (octacyanomolybdate(V)) which has a similar oxidizing potential ( $E^0 = +0.73$  volts versus the saturated calomel electrode<sup>9</sup>).

Potassium molybdicyanide was used by Kratochvil and Diehl<sup>10</sup> to titrate cobalt(II) in ammoniacal media. While they obtained good results the procedure was limited by the need to constantly standardize the titrant because of its poor stability to light. They therefore coulometrically titrated cobalt(II) in the 2.7 to 27 mg range by generating the molybdicyanide from the more stable tetravalent molybdenum compound, potassium molybdocyanide. The end point was determined potentiometrically. Hernandez-Mendez and Lucena-Conde have also used coulometrically generated molybdicyanide to determine ferrocyanide<sup>11</sup> and thallium<sup>12</sup>. In the 1 to 20  $\mu$ eq ferricyanide range they obtained results having a standard deviation of only 3 ppt. The titration was not affected by moderate amounts of acid or base but at pH 1 no potential break was observed and above pH 13 high results were found, probably due to the oxidation of water. The potential required for the oxidation of water is only 0.36 volts at this pH.

Molybdicyanide has been used previously by Vincente-Perez and Cordova-Orellana<sup>13</sup> to titrate cerium(III) in the 70 to 700 mg range. They adjusted the pH of a 50 percent carbonate solution



to 6 to 6.5 and boiled the solution to remove dissolved oxygen. After cooling to room temperature the titration with 0.02 to 0.1M molybdicyanide was performed in artificial light. The following study is an extension of this work to the coulometric determination of smaller quantities of cerium(III).

Coulometric titrations are analyses that use electrons as the titrant<sup>14</sup>. A measured constant current is passed through a solution to oxidize or reduce the compound under investigation. As the concentration of the reacting species becomes low concentration polarization occurs and the resulting increase in electrode potential causes reactions involving other species present in the solution. The current efficiency in terms of the reacting species therefore falls below 100 percent and high results are obtained. This problem is avoided by adding a large excess of a reagent that is electrochemically oxidized at a higher potential than that of the substance being determined. This reagent in its oxidized form acts as a conventional oxidizing agent to oxidize the reacting species. Providing this reaction is fast and complete the current efficiency for the overall reaction can be maintained at 100 percent. Although the intermediate formed is frequently referred to as an electrochemically generated titrant, this term is slightly misleading since the titrant is really the electron. A variation of coulometric analysis involves generation of the oxidizing intermediate in an external solution and addition to the cell at a constant rate. In this case the terms "electrochemically generated" titrant or "coulometrically generated" titrant are acceptable. However common usage allows these terms to cover both internally and externally generated intermediates, so they will be used here to describe the molybdicyanide species.



## APPARATUS AND REAGENTS

### COULOMETER CELL

The coulometric cell (Figure 1) was a 150 ml beaker around which black plastic tape was horizontally wrapped to exclude light. A vertical window about one half inch wide was cut in this tape over which a removable length of tape was placed during an analysis. This window served two purposes; it enabled visual observation of the cell interior to check stirring and nitrogen flow rates, and it allowed accelerated photodecomposition of unwanted excesses of molybdicyanide, thereby reducing the time between successive runs in a given solution.

The cell contained four electrodes, two for current generation and two for potentiometric end point detection. Both generating electrodes were cylindrical platinum gauzes. The anode dipped directly into the reaction solution while the cathode was in a compartment separated by a glass frit. This compartment contained 50 percent potassium carbonate. The potential measuring electrodes were a platinum wire indicating electrode wrapped around a saturated calomel reference electrode. The electrodes and an inlet for the nitrogen, which was constantly bubbled through the solution to exclude oxygen, were held in a rubber stopper which also prevented light entering through the top of the cell. The solution was stirred magnetically.

The current source for the earlier experiments was a Sargent Model IV Coulometric Analyzer. The lowest current range available on this instrument was only 5 mA, so the majority of the work was done with a Leeds and Northrup Coulometric Analyzer using the 6.43 and 0.643 mA settings.

The cell potential was observed either visually with a Beckman Zeromatic pH Meter or recorded with a Metrohm Model E436 Potentiograph in the mV or dE/dt modes.





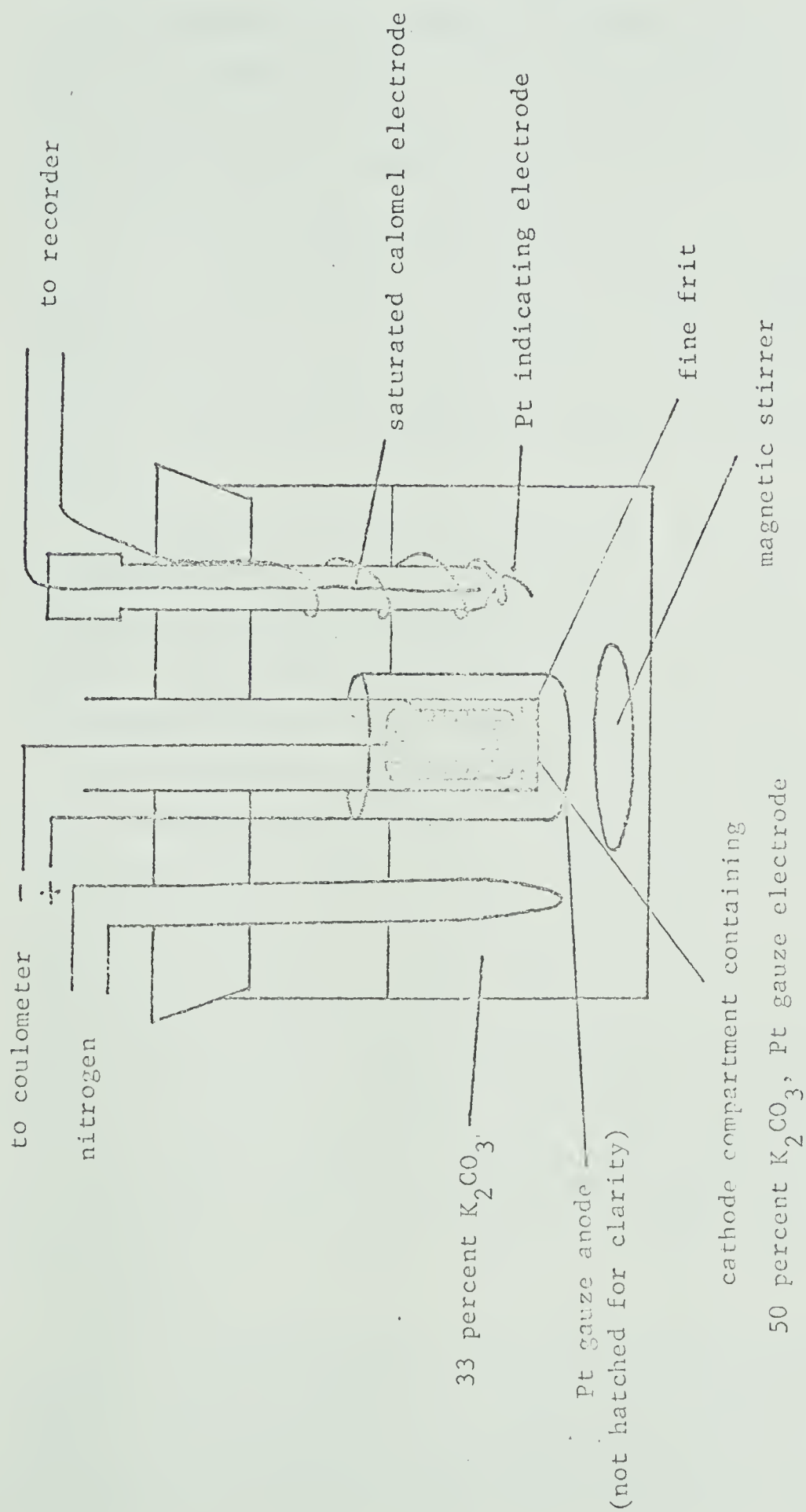


Figure 1 Cell Used in Coulometric Titrations



## REAGENTS

### Preparation of Potassium Molybdocyanide

The preparation of potassium molybdocyanide is based on the method of Furman and Miller <sup>15</sup> with few alterations. In view of the extremely toxic nature of many of the chemicals employed in this preparation all work was carried out in a fume hood and rubber gloves were worn at all times.

In a 4-litre beaker 200 g (1.384 moles) of molybdenum(VI) trioxide was dissolved in a solution of 160 g (3.056 moles) of potassium hydroxide in 400 ml of water. Then 1 litre of concentrated hydrochloric acid was slowly added with constant stirring. The final solution was heated on a steam bath for one half hour.

A concentrated solution of potassium thiocyanate was prepared by dissolving 600 g (6.18 moles) in 600 ml of water. This solution was added with constant stirring to the hot molybdic acid solution. The resulting deep red solution was diluted with 1200 ml of water and heated on a steam bath for two hours.

The solution was filtered while still hot through a celite bed in a steam-jacketed Büchner funnel and the filtrate was transferred to a 4-litre beaker. It is important to avoid washing the filter bed at this stage since any product in it will immediately hydrolyze and wash water entering the filtrate may cause hydrolysis there as well. Pyridine (260 to 300 ml) was added slowly to the filtrate with constant stirring until a yellow solid began to separate. The beaker was then placed in an ice bath until the reddish-black oily layer became very viscous. The supernatant liquid, which was still slightly red in colour, was decanted and the product washed twice with water by decantation.

The tarry residue was treated with a solution of 800 g of potassium cyanide in 1200 ml of water. The compound dissolved readily to form a green then yellow-brown solution. The solution was heated on a steam bath with frequent stirring for one half hour. The hot solution was filtered by suction through



a steam-jacketed Büchner funnel to remove some black residue from the solution. The filtrate was returned to its original beaker and evaporated on the steam bath until the volume had been reduced by 50 percent. The solution was cooled in an ice bath and the blackish-brown crystals were filtered off.

The crude product was dissolved in a minimum of hot water (about 70°C), charcoal was added to decolorize the solution, and it was filtered through a celite bed in a steam-jacketed Büchner funnel. Slowly one to two volumes of ethanol were added to the cooled filtrate. The golden-yellow crystals were filtered and washed with ethanol and ether.

This charcoal treatment was repeated twice. The final product was air-dried and stored in a dark bottle. The yield of  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  was about 270 g (40 percent of theoretical).

The exact steps in this synthesis cannot be represented by balanced equations. It has been suggested by Furman and Miller that a soluble oxythiocyanate complex of molybdenum is formed as an intermediate. This complex gives an adduct with pyridine which separates as a reddish-black tarry solid. The final step is complete ligand replacement on the molybdenum with cyanide ions, with simultaneous reduction of the molybdenum from the +6 to the +4 oxidation state.

#### Analysis of Potassium Molybdocyanide

Although molybdicyanide will oxidize cerium(III) in alkaline solution the potential of the molybdenum(V)/molybdenum(IV) couple does not change significantly with pH. It is therefore possible to oxidize molybdocyanide to molybdicyanide with cerium(IV) in acid solution. This property serves as a basis for the analysis of molybdocyanide.

Approximately 1.2 g of molybdocyanide (2.4 mmoles) was dissolved in 50 ml of 1M sulphuric acid. This solution was titrated with a cerium(IV) solution which had previously been standardized against primary standard arsenic trioxide (Fisher Scientific Co.). The intense yellow colour of the solution ruled





out an indicator end point and so the end point was determined potentiometrically using a platinum wire indicating and a saturated calomel reference electrode.

Two samples of air-dried molybdocyanide were analyzed. Both gave a result of 99.25 percent as the dihydrate. When the molybdocyanide was dried in a vacuum the results were invariably high indicating partial dehydration. Therefore vacuum drying of the compound is not recommended.

#### Preparation and Analysis of Standard Cerium(III) Solution

An approximately 0.1M cerium(III) solution was prepared by dissolving about 35 g cerous nitrate hexahydrate (Fisher Purified Grade) in 30 ml of sulphuric acid. Water was slowly added, with constant stirring to avoid hydrolysis, until the volume was around one litre.

The solution was analyzed by oxidizing the cerium(III) to cerium(IV) with ammonium persulphate in the presence of silver nitrate as catalyst according to the method of Willard and Young<sup>16</sup>. A 25 ml aliquot of the cerium(III) solution was transferred to a beaker. A 10 ml portion of concentrated sulphuric acid was added and the solution was diluted to 150 ml with water. Next 10 ml of silver nitrate solution (0.25 g/100 ml) and 5 g of ammonium persulphate were added and the resulting solution was boiled for 30 to 40 minutes. It is necessary to cover the beaker with a watch glass during the heating stage because decomposition of the persulphate causes a fine spray of the solution to spit out of the unprotected beaker. After cooling to room temperature the solution was titrated with 0.1M ferrous ammonium sulphate using ferroin as indicator. The ferrous ammonium sulphate solution was standardized immediately prior to this titration with the same standard cerium(IV) solution used in the analysis of the potassium molybdocyanide.

From this analysis the cerium(III) concentration was found to be 0.1202M (standard deviation 1 ppt for 6 determinations). This solution was used throughout the following work.



Since a measured weight rather than volume of this solution was used for some of the later work, its density was determined by weighing an accurately pipeted 25 ml portion. The density was found to be 1.0661 at 25°C (i.e. 0.1128 mmoles/g) when initially made up and 1.0664 at 25°C after four months.

#### Other Reagents Used

Ceric ammonium sulphate and ceric ammonium nitrate were both used as received from Fisher. Anhydrous potassium carbonate was obtained from B.D.H. (Analar and Reagent Grades) and Shawnigan. No difference was noticed in the results with the grade or supplier of the carbonate.

All other chemicals were reagent grade and were used without further purification.



### EXPERIMENTAL PROCEDURE

In a typical experiment 20 g of potassium carbonate (2.4M) and 0.4 g of potassium molybdicyanide (0.8 meq) were dissolved in 60 ml of water in the cell. The counter electrode compartment was partially filled with 50 percent potassium carbonate. About 50  $\mu$ l of deaerated cerium(III) solution was then added to the cell and the current was switched on (6.43 mA-range). An excess of molybdicyanide, as indicated by a rise in the cell potential to around +450 mV, was generated. This run served as a blank and was necessary to oxidize any impurities present in the solution. If this blank run was omitted the first one or two analyses were almost always higher than the subsequent runs. As soon as the current was switched off the cell potential began to drift downward because of decomposition of the molybdicyanide. When the potential had dropped to between +50 and +150 mV (the exact value depended on the end point detection technique used and the amount of cerium(III) added) a measured sample of cerium(III) was injected into the solution. For small samples of cerium (1 to 6  $\mu$ eq) a known volume of solution was added from a microsyringe while larger samples were weighed. Addition of the cerium(III) caused the potential to drop to between -100 and -250 mV. Generation of molybdicyanide was started as soon as the potential reached a steady minimum value. The potential was monitored throughout the titration and the end point was determined by one of the following techniques:

- 1) Initially the potential was recorded as a function of the quantity of current passed (Figure 2). The end point was taken either as the midpoint of the break or as the initial potential prior to addition of the cerium(III) sample. The asymmetry of the potential break in the 0.643 mA current range made location of the end point difficult. A set end point potential could not be used because of the equivalence point variation from run to run. The method was time consuming since individual analysis of



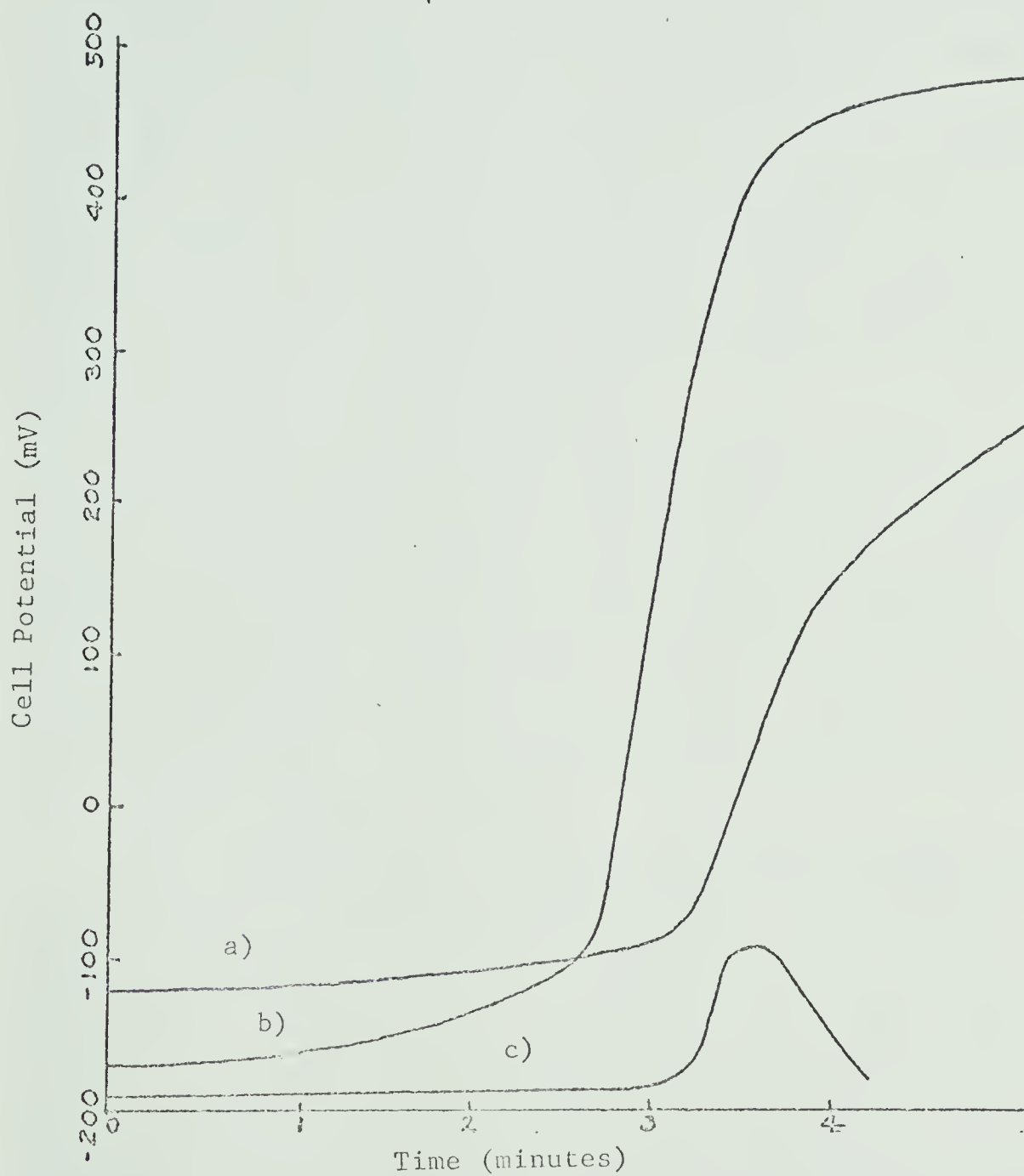


Figure 2 Potential versus Time of Current Generation  
a) 1.20  $\mu\text{eq}$  at 0.643 mA current  
b) 10.0  $\mu\text{eq}$  at 6.43 mA current  
curve c) is a  $dE/dt$  plot of curve a)





each titration curve was required. This technique proved useful when a new system or interference was being studied, however.

2) The drawbacks of the above technique were largely overcome by an adaption of the end point detection method employed by Hernandez-Mendez and Lucena-Conde in their coulometric analysis of ferrocyanide. Before each analysis they added a small quantity of ferrocyanide and titrated the solution to a potential near the equivalence point. A sample was added and titrated back to the original potential. It was found more convenient in this work to generate an excess of molybdcyanide allow it to decompose until the cell potential was near the equivalence point and then to titrate back to the same potential.

Best results were obtained when the current was switched on and off in short bursts near the end point because the potential continued to climb after generation had been stopped. About thirty seconds was required after each current interruption before the potential became steady. At a current of 6.43 mA the potential rose about 60 mV for each 0.1  $\mu$ eq of current passed in the end point region. With practice it was possible to choose the end point to within 0.02  $\mu$ eq.

3) The rate of change of potential could be recorded using the dE/dt mode of the Metrohm potentiometer. The recording (Figure 2) appeared as a slowly rising line prior to the end point with an asymmetric hump as the potential changed rapidly in the end point region. The end point was taken as the maximum rate of change of potential, that is the summit of the hump. The summit was often quite rounded and so the location of the end point was again suspect. The reproducibility of this technique was quite good and was the most satisfactory at low current range.

For samples containing less than 6  $\mu$ eq of cerium(III) as many as fifteen analyses could be performed sequentially in the same carbonate solution. In higher concentration ranges results became erratic after about six samples had been analyzed. If a gap of more than thirty minutes was allowed between analyses it was necessary to reject the first result after the break as a blank.



## RESULTS AND DISCUSSION

### STUDY OF EXPERIMENTAL CONDITIONS

The experimental conditions for this work had been roughly defined by the earlier observations of Tomicek and Hernandez-Mendez. Tomicek's results indicated that to avoid precipitation of cerium(III) the carbonate concentration should be well above 20 percent. Since his work covered cerium concentrations much greater than those studied in this work more dilute carbonate solutions could perhaps be tolerated here. The main reason for keeping the carbonate concentration as low as possible is to prevent the pH of the system becoming too high. When Hernandez-Mendez analyzed ferrocyanide by coulometrically generated molybdocyanide he obtained high results when the pH was greater than 13. Although his results may not apply in this work since he used an ammonia buffered solution, it appeared advisable to keep the pH as low as possible by using more dilute carbonate solutions. Alternatively potassium bicarbonate could be added to reduce the alkalinity of the system.

Hernandez-Mendez used 0.07 g of potassium molybdocyanide (0.14 meq) in his solutions when determining ferrocyanide samples in the 1 to 20  $\mu$ eq range. This seems a rather small excess of the molybdocyanide. If the molybdocyanide is not efficiently reduced back to molybdocyanide on reaction the concentration of the latter may become too low for 100 percent current efficiency after five or six 20- $\mu$ eq samples have been oxidized in the same solution. A larger amount of molybdocyanide would avoid this problem. The alternative would be to use fresh solutions each time, but this is a less satisfactory approach because of longer times and the excessive consumption of potassium molybdocyanide required.

An initial survey was therefore performed to determine the sensitivity of the titrant to light, and to establish optimum levels of carbonate, bicarbonate, molybdocyanide, and current.



### Light Sensitivity of the Titrant

The sensitivity of molybdocyanide to light was briefly mentioned earlier. It was hoped that electrogenerated molybdocyanide would react with cerium(III) in the cell before decomposition occurred. However, in solutions exposed to light the break was small, poorly defined, and occurred only after a 2 to 3-fold excess of current had been passed. Aluminum foil wrapped around the cell increased the current efficiency and sharpened the break. The best results were obtained with the tape-covered cell described in the apparatus or with a cell sprayed with black paint. The latter was not used because of a tendency for the paint to flake during use.

### Potassium Carbonate and Potassium Bicarbonate Concentrations

No trend was established as the concentration of potassium carbonate was increased (Table I). The cerium(III) found was about 18 percent high at all carbonate concentrations examined. High results were found in all the following experimental work. In a carbonate range from 20 to 40 percent potassium carbonate the change in pH is from 12.23 to 12.38, so this should not be a significant factor. The important point made by this study was the poor reproducibility obtained in the 20 to 40 percent potassium carbonate solutions. This cannot be attributed to variations in sample size, as the samples were added from a microliter syringe having a precision of around 1 percent. It was therefore decided to use 33 percent potassium carbonate solutions throughout the following work. This ensured a carbonate concentration well above the 20 percent level even after the solution had been diluted by several cerium samples.

For the work on solutions containing bicarbonate, samples were injected into the cell from a 1-ml syringe which was weighed before and after the addition. All solutions contained 20 g potassium carbonate and 0.4 g potassium molybdocyanide in 60 ml of water. The sample size was not constant because it was



TABLE I  
Effect of Potassium Carbonate Concentration  
on Cerium(III) Analysis

K <sub>2</sub> CO <sub>3</sub> concentration (percent)	Cerium(III) found* µeq	Standard Deviation	
		absolute	relative
20	2.75	0.18	6.5
25	2.82	0.03	1.1
33	2.83	0.02	0.7
40	2.81	0.10	3.5

Cerium(III) added: 2.40 µeq each analysis

\*Each value is the average of 6 determinations.

TABLE II  
Effect of Potassium Bicarbonate  
on Cerium(III) Analysis

KHCO <sub>3</sub> conc. (percent)	pH of solution	Percentage of Cerium(III) found*	Stan. Dev.
0	12.37	103.0	1.1
4	11.18	104.1	0.6
8	10.78	105.1	0.7

Cerium(III) sample size 12 to 16 µeq

\*Each value is the average of 5 determinations.





impossible to inject exactly reproducible portions of sample from the 1-ml syringe used. Therefore results were compared on a basis of the percent cerium(III) recovered (Table II).

The data tabulated in Table II shows that results were higher as the bicarbonate concentration increased. This trend is opposite to that expected if it is assumed that high pH decreases the stability of molybdicyanide. Apparently the increased stability of molybdicyanide at lower pH values is offset by one or more undetermined factors. In view of these results bicarbonate was not used further. It should be noted that some bicarbonate is formed in the cell solution whenever acidic cerium(III) sample solutions are added. With small sample sizes however this does not give an appreciable bicarbonate concentration.

One experiment was run to determine the effect of potassium hydroxide on the titration. On addition of cerium(III) to a solution of 0.4M potassium hydroxide in 33 percent potassium carbonate the potential dropped to -550 mV, well below the value observed in straight carbonate solutions. No clear break was found in the titration curve. The potential rose to about +80 mV after a 100 percent excess of current had been passed, and the solution contained a white precipitate, probably cerium(III) hydroxide.

#### Potassium Molybdocyanide Concentration

The exact concentration of the molybdocyanide used should not affect the results of the cerium(III) analyses providing that it is always in excess. The results in Table III show no significant variation in accuracy with molybdocyanide concentration, although the standard deviation in the results increases as the concentration of molybdocyanide increases. Since in this experiment successive portions of molybdocyanide were added to the same carbonate solution, by the time the final analyses were performed this solution probably contained numerous reaction and decomposition products. This factor,



TABLE III  
Effect of Potassium Molybdocyanide Concentration  
on Cerium(III) Analysis

Wt. Potassium Molybdocyanide taken		Cerium(III) found*	Standard Deviation	
g	meq	µeq	absolute	relative
0.2	0.4	2.84	0.01	0.4
0.4	0.8	2.79	0.01	0.4
0.6	1.2	2.85	0.03	1.1
0.8	1.6	2.82	0.06	2.2

Cerium(III) sample size 2.40 µeq

\*Each value is the average of 3 determinations.



rather than the molybdocyanide concentration, may have lowered the precision. The concentration of molybdocyanide chosen for subsequent work was 0.4 g (0.8 meq) in 60 ml. In this solution there is still a large excess of molybdocyanide after six 50  $\mu$ eq cerium(III) samples and a blank have been titrated.

#### Current Range

The magnitude of the current used to generate the molybdicyanide greatly affects the size and shape of the potential break in the titration (Figure 2). At the higher current range, 6.43 mA, the break is about 600 mV and slightly asymmetric. Since the cerium(IV)/cerium(III) couple has been shown to be reversible in carbonate solutions <sup>7</sup> the asymmetry may result from the instability of the molybdicyanide species. The equivalence point taken was +130 mV versus the saturated calomel electrode. At the lower current range, 0.643 mA, the potential break was much smaller and very asymmetric. The steepest part of the break ends at about +150 mV, but the potential continues to rise slowly and constantly to the same value found at the 6.43 mA range. This asymmetry may be caused in part by decomposition of the molybdicyanide, since at the lower current range molybdicyanide is being generated only slightly faster than it is decomposing. This will produce a slow rise in potential after the cerium(III) has been completely oxidized. Molybdicyanide decomposition should not be a problem providing the reaction with cerium(III) is sufficiently faster than the decomposition.

Molybdicyanide is generated at a rate of one  $\mu$ eq per two and one half minutes at the 0.643 mA level. At this rate approximately 20 minutes is required to titrate a 6  $\mu$ eq cerium(III) sample, including generation past the equivalence point to define the titration break. Samples larger than 6  $\mu$ eq were titrated at the 6.43 mA level to avoid excessive analysis times. Attempts were made to use the higher current range during early stages of the titration, then switch to the 0.643 mA level in the end point region. These attempts were largely unsuccessful because of the



difference in equivalence points (Figure 2). When the titration is 95 percent complete at the 6.43 mA current the potential is about +50 mV which is the end point at the 0.643 mA current. Where end points could be established no improvement in precision was found.

The recommended optimum procedure for the titration can be summarized as follows (see Experimental Procedure). A solution of 20 g of potassium carbonate and 0.4 g of potassium molybdocyanide in 60 ml of water is added to the coulometer cell. The cell is covered with black tape to exclude light. The solution is deaerated with nitrogen to prevent oxidation of the cerium(III) by dissolved oxygen. Cerium(III) samples smaller than 6  $\mu$ eq are injected into the solution with a microliter syringe. Larger cerium(III) samples are weighed into the solution from a 1-ml syringe. The amount used to generate the molybdicyanide is 0.643 mA for cerium(III) samples of less than 6  $\mu$ eq and 6.43 mA for cerium(III) samples in the 6 to 50  $\mu$ eq range.

#### ACCURACY AND PRECISION OF METHOD

Once standard conditions had been established the accuracy and precision of the method was assessed. The results will be discussed in two parts depending on the current used.

At 0.643 mA all results were high by a fairly constant value. Table IV shows the range of results found when 1.20  $\mu$ eq samples were analyzed successively in the same solution. The mean error of +0.15  $\mu$ eq is 13 percent high with a standard deviation of 3 percent. As only 10  $\mu$ l of the cerium(III) solution was added from a microsyringe the standard deviation is in the expected order. The high results may be caused by decomposition of molybdicyanide. The error is close to a constant value of +0.20  $\mu$ eq over the range of 1 to 6  $\mu$ eq (Table V). These results were obtained by analyzing successive 10, 20, 30, 40 and 50  $\mu$ l samples in a cell solution, then





TABLE IV  
Reproducibility of Cerium(III) Analyses  
at 0.643 mA Current

Cerium(III) found	Error
$\mu\text{eq}$	$\mu\text{eq}$
1.35	+0.15
1.36	+0.16
1.35	+0.15
1.28	+0.08
1.34	+0.14
1.37	+0.17
<u>1.42</u>	<u>+0.22</u>
Average 1.35	+0.15

Standard Deviation: 0.04 absolute; 3.0 relative

Sample size taken: 1.20  $\mu\text{eq}$

All analyses performed consecutively in the same solution.

TABLE V  
Precision and Accuracy of Cerium(III) Analyses  
at 0.643 mA Current

Added	Found*	Mean Error	<u>Stan. Dev.</u>	
			abs.	rel.
1.20	1.40	+0.20	0.08	5.7
2.40	2.63	+0.23	0.03	1.1
3.61	3.83	+0.22	0.06	1.6
4.81	4.96	+0.15	0.04	0.8
6.01	6.14	+0.13	0.22	3.6
6.01	6.20	+0.19	0.09	1.5

\*Each value is the average of 6 determinations.



repeating this series twice more in the same solution. The whole experiment was repeated a second time in a fresh solution to give a total of 6 values for each point. The standard deviation obtained for the 6.01  $\mu$ eq samples was considerably greater than for any of the other samples, so a series of 6 analyses of this sample size was made in a separate solution. These results, included in Table V, indicate that precision comparable to smaller sample sizes can be attained.

The determinate error in the results can be explained on the basis of decomposition of molybdicyanide in the following way. During the early stages of the analysis cerium(III) is oxidized directly at the electrode. As the cerium(III) concentration decreases molybdocyanide begins to be oxidized also. Oxidation of the cerium(III) by the generated molybdicyanide then takes place. Some of the molybdicyanide decomposes however before it can react with cerium(III) and so more current than necessary to oxidize the cerium(III) is required. Since molybdicyanide is generated primarily at low cerium(III) concentrations during the titration, that is, near the end point, a relatively constant amount of molybdicyanide may decompose during each analysis independent of the amount of cerium(III) taken. This will cause a positive determinate error in the results.

With 6.43 mA generating current, sample sizes were chosen in the following ranges: 5 to 9  $\mu$ eq, 13 to 17  $\mu$ eq, and 25 to 30  $\mu$ eq. Direct comparison of individual results cannot be made because samples varied in size. Table VI illustrates the spread found in the analysis of a series of samples in the same solution. The error is considerably larger than that found at 0.643 mA. By averaging the cerium(III) added and found within the above sample ranges a rough idea of the error observed can be made (Table VII). It can be seen that the error is not constant as was found at the lower current range. A least squares analysis of forty experimental results in which the cerium(III) found was plotted against cerium(III) added was performed by computer. The slope



TABLE VI  
Reproducibility of Cerium(III) Analyses  
at 6.43 mA Current

Cerium(III) Added	Cerium(III) Found	Error
$\mu\text{eq}$	$\mu\text{eq}$	$\mu\text{eq}$
29.17	29.87	+0.70
26.62	27.27	+0.65
25.60	26.31	+0.71
27.43	27.99	+0.56
26.25	26.96	+0.71
26.27	26.80	+0.53

TABLE VII  
Accuracy of Cerium(III) Analyses  
at 6.43 mA Current

Cerium(III) Range	Mean Cerium(III) Added	Mean Cerium(III) Found	Mean Error
$\mu\text{eq}$	$\mu\text{eq}$	$\mu\text{eq}$	$\mu\text{eq}$
5 to 9	7.32	7.54	+0.22
12 to 17	15.04	15.48	+0.44
25 to 30	26.94	27.43	+0.49



of the line should be 1.000 and the intercept should give the determinate error. The least squares analysis gave a slope of 1.011 with a standard deviation of 0.003 and an intercept of 0.25  $\mu$ eq. The value of the slope is slightly higher than that predicted; this suggests that decomposition of the molybdicyanide may be taking place throughout the titration, and not just at or near the end point. This could be possible if some concentration polarization of the electrode begins very soon after the titration is begun. Once the cerium(III) concentration reaches the same minimum value as at the lower concentration constant decomposition occurs. This statement is supported by the closeness of the intercepts found with the two current ranges: 0.25  $\mu$ eq at 6.43 mA and 0.22  $\mu$ eq at 0.643 mA.

Since a linear relationship is seen between the amounts of cerium(III) added and found, the analysis of an unknown can be performed using a standard calibration curve. An example of such a calibration curve at 0.643 mA is shown in Figure 3. A similar plot was obtained at 6.43 mA.

In summary, to determine cerium(III) by this method a preliminary analysis should be run on the cerium(III) unknown to find the range of standards required. Three or four coulometric titrations should then be run and the average read off a calibration curve.

#### INTERFERENCES

##### Cerium(IV)

A stock solution of cerium(III) containing cerium(IV) was prepared by diluting 3 ml of 0.1M cerium(III) nitrate to 25 ml with 0.1M ceric ammonium sulphate solution. Each ml of the stock solution contained 14.41  $\mu$ eq of cerium(III).

By means of a 1-ml pipet aliquots of the stock solution were added to the cell. Initial results were higher than expected, indicating that an oxidizable impurity might be present in the cerium(IV) solution. A blank containing 1 ml of the 0.1M





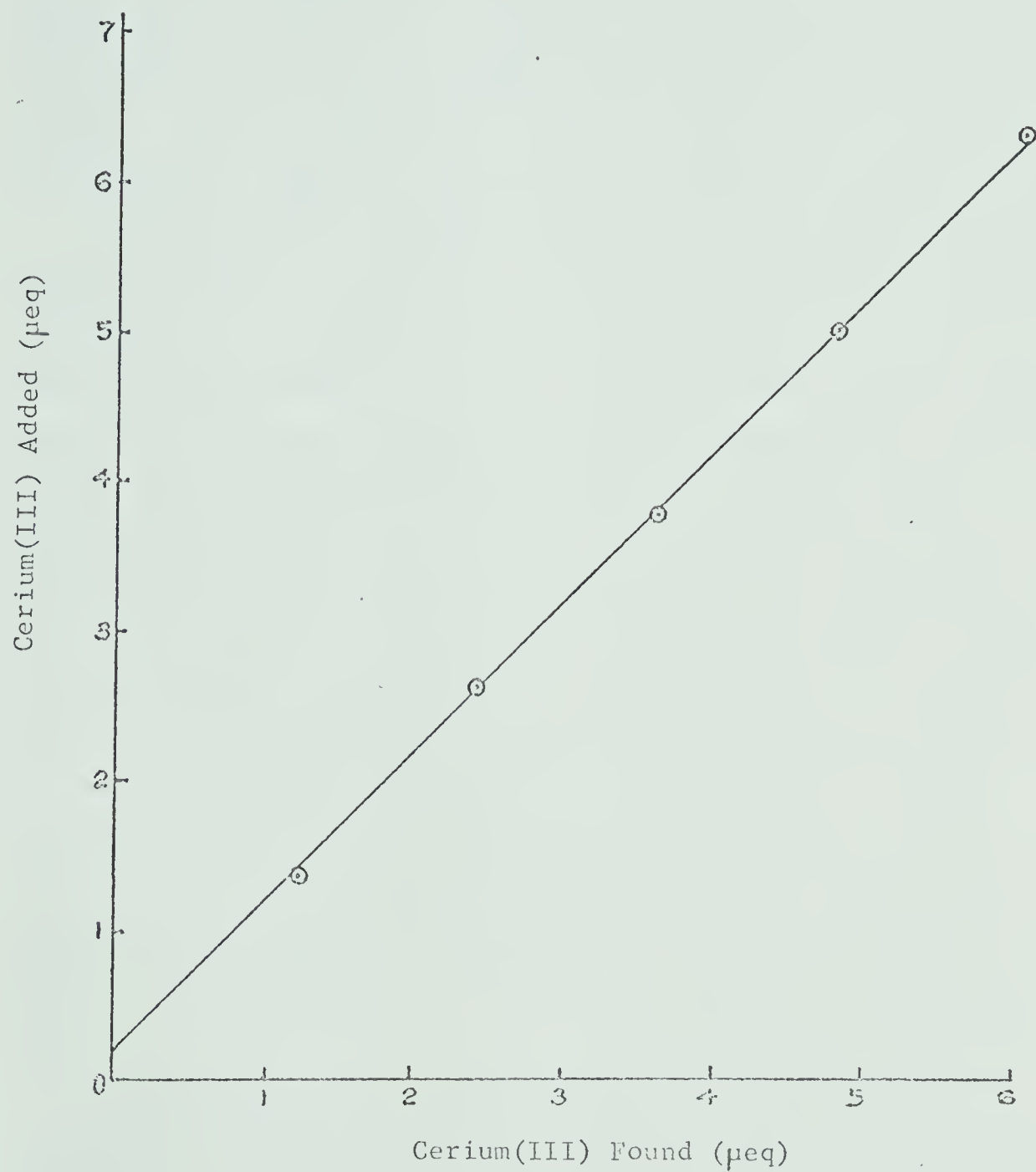


Figure 3 Calibration Curve for Cerium(III) Analysis

This is an example of a typical calibration curve at the 0.643 mA current range. Calibrations at the 6.43 mA range were similar in appearance.



cerium(IV) solution required about 0.75  $\mu$ eq of current to reach the usual end point potential. After this blank was subtracted from the titration values the amount of cerium(III) recovered was within the anticipated range. The results of this work are summarized in Table VIII. Two blank runs were made for each group of analyses and the mean of these blanks was subtracted from the results. From a calibration curve, the mean corrected quantity of cerium(III) found was 14.80  $\mu$ eq; the amount taken was 14.4  $\mu$ eq.

The oxidizable substance most likely to be present in ceric ammonium sulphate solutions is cerium(III). The concentration of cerium(IV) was 0.1048M by titration with arsenic trioxide. Therefore approximately 0.7 percent of the total cerium in the solution was in the trivalent state if we assume that cerium(III) is the only oxidizable substance present. A 25-ml aliquot of the cerium(IV) solution was analyzed for total cerium by treatment in the manner described earlier for the oxidation of cerium(III). After oxidation the solution was titrated with standard ferrous ammonium sulphate. The results of this analysis are included in Table IX. They show that after oxidation the cerium(IV) content of the solution has risen by 0.6 percent, which is in good agreement with the value indicated coulometrically. As the results of the titrations with ferrous ammonium sulphate were so close to each other a statistical analysis was made which confirmed that there was a difference between the two sets of data.

A crosscheck of the total cerium content in the standard cerium(IV) solution was made as follows. Approximately 3 g of the cerium solution was accurately weighed out. One drop of 30 percent hydrogen peroxide was added to reduce the cerium(IV) to cerium(III). After boiling to remove excess peroxide the cerium(III) was titrated with EDTA following the method of Fritz, Lane and Bystroff<sup>17</sup>. A 1 ml portion of a standard solution of copper(II) (0.007914M) was added to the solution. A few drops of pyridine were used to buffer the solution at around pH 6. After



TABLE VIII  
Cerium(III) Analyses  
in the Presence of Cerium(IV)

Cerium(III) found $\mu\text{eq}$	No. of Determinations	Mean Blank $\mu\text{eq}$	Cerium(III) corrected $\mu\text{eq}$
15.77	3	0.84	14.93
15.62	4	0.64	14.98
15.68	2	0.68	15.00
15.61	5	0.83	14.78
15.33	5	0.80	14.53

Cerium(III) added: 14.41  $\mu\text{eq}$

Mean Cerium(III) found: 14.80  $\mu\text{eq}$

Mean blank: 0.76  $\mu\text{eq}$

Standard Deviation: 0.27 absolute; 1.8 relative

TABLE IX  
Determination of Cerium(III)  
in Ceric Ammonium Sulphate

Analytical Method	Cerium(IV)	Total Cerium	Cerium(III) (percent)
Coulometry	-	-	0.7
Titration with Fe(II)	0.1048M	0.1054M	0.6
Titration with EDTA	-	0.1056M	0.8*

\*Assuming cerium(IV) concentration is 0.1048M



dilution to about 100 ml with water the cerium(III) was titrated with standard EDTA using 2 drops of 0.05 percent naphthyl azoxine S indicator. A blank run without the cerium(IV) was performed and required 2.70 ml of EDTA. This volume was subtracted from the above titration results. Even with copper(II) present to improve the colour change the end point was not very distinct, the colour changing from yellow through orange to a pure red. However the method gave a relative standard deviation of 4 ppt for 3 analyses. The total cerium(III) concentration found by this procedure was 0.1056M. This value is 0.8 percent higher than that expected if no cerium(III) were present in the cerium(IV) originally.

A sample of ceric ammonium sulphate, the label of which reported a purity of 95.2 percent, was found to contain approximately 0.7 percent cerium(III). This value was verified by two independent methods. Coulometric analysis of a sample of ceric ammonium nitrate (99.8 percent) gave 0.25 percent cerium(III). This amount was too small to be confirmed by the alternative procedure used above.

In summary, the above work confirms that the proposed coulometric method for the analysis of cerium(III) can be used in the presence of large amounts of cerium(IV). Less than 1 peq of cerium(III) could be estimated in a one hundred-fold excess of cerium(IV).

#### Other Interferences

Approximately 0.1M solutions of the following metal ions were prepared: lanthanum(III), vanadium(IV), cobalt(II), iron(II), iron(III), nickel(II), chromium(III), manganese(II), zinc(II), and copper(II). Stock titration solutions containing these cations were prepared by mixing an equal volume of the stock cerium(III) solution with each of these solutions. The effect of each interference was investigated independently using the following procedure. A pretitration of 50  $\mu$ l of cerium(III) was made. Next a 20- $\mu$ l sample of cerium(III) was analyzed to ensure that the system was working satisfactorily. Then the following





solutions were titrated in order: 20  $\mu$ l of the 0.1M interference; 20  $\mu$ l of cerium(III); and 40  $\mu$ l of the stock cerium(III)/interference solution. If the interference had no effect on the cerium(III) analysis at this concentration a large excess (0.1 to 0.2 ml) of the interference was added and another 20  $\mu$ l cerium(III) sample was analyzed.

Of the above cations only lanthanum, nickel, zinc, and iron(III) had no effect on the cerium analysis at equimolar concentrations. Iron(III) interfered at higher concentrations owing to precipitation of ferric hydroxide, which coated the electrodes and reduced the current efficiency. The remaining ions, with the exception of copper(II), interfered because they were oxidized along with cerium(III) under the conditions used. Manganese(II) was oxidized in one step to manganese dioxide; chromium(III) in two steps to chromate. The others increased their oxidation number by one. Cerium(III) could still be estimated in solutions containing chromium(III) and cobalt(II) since the potential break at the cerium end point was complete before oxidation of the interferences began. However the break tended to be more drawn out and the precision and accuracy were decreased.

The presence of copper(II) ions in the solution being titrated had an extremely marked effect on the system. On addition of copper the potential rose to +180 mV and no break was observed upon titration. After titration the potential would not drop below +130 mV. Addition of cerium(III) at this point lowered the value from 130 mV to about -20 mV, but on titration no well defined potential break occurred. One possible explanation for this result is that copper(II) reacts with free cyanide ions in the solution to form a complex cyanide. This insoluble complex forms a coating on the indicating electrode which then fails to monitor the potential accurately.



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